Swelling and Shrinking of Polyelectrolyte Microcapsules in Response to Changes in Temperature and Ionic Strength

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Abstract: Swelling and shrinking of polyelectrolyte microcapsules consisting of poly(styrene sulfonate, sodium salt) (PSS) and poly(diallyldimethyl ammonium) chloride (PDADMAC) multilayers have been observed in response to temperature and electrolyte exposure, respectively. Heat-induced capsule swelling and capsule wall volume reduction were observed by confocal laser scanning microscopy (CLSM) and scanning force microscopy (SFM). On the other hand, pronounced shrinking in diameter induced by exposure to an electrolyte was observed in parallel to increases in the thickness of the capsule wall. The estimated wall volume was reduced to two thirds of the control for the salt-exposed capsules and one half for the salt-exposed and simultaneously annealed capsules. This reduction in volume was supposedly mainly caused by the compression of the capsule wall due to the ionic screening from the electrolyte. The highly porous microstructure of the multilayers and loosely bound PSS/PDADMAC complex are thought to be responsible for the structure of the PSS/PDADMAC capsules being easily modulated upon annealing and salt-exposure.

Keywords: capsules · colloids · layered compounds · polyelectrolytes · self-deposition

Introduction

The layer-by-layer (LBL) self-assembly technique has been diversely applied to fabricate multilayer ultrathin organic or hybrid films with various properties since it was introduced by Decher et al.[1] Oppositely charged polyelectrolytes from dilute aqueous solution are consecutively deposited onto solid substrates by utilizing the electrostatic attraction and complex formation between polyanions and polycations. The majority of studies have thus far focused on film formation on macroscopically flat substrates, for example, silicon, glass, and gold wafers.

Recently novel nano- and micrometer-sized capsules have been prepared by applying this LBL technique to sacrificial colloidal templates, followed by decomposition of the cores.[2] Capsules with a given size and a given number of polyelectrolyte layers including biopolymers, lipids, surfactants or/and nanoparticles and derived from different templates have been fabricated.[3] These capsules were characterized with respect to their morphology, surface charge, stability, elasticity, capacitance, conductance and permeability.[4–7] Nowadays these Nano- and micron-sized polyelectrolyte capsules are increasingly interesting because of their potential applications as new colloidal structures in areas such as medicine, drug delivery, and, for example, catalysis.

Many efforts have been devoted to the nanoscale encapsulation of drugs, minerals, dyes, proteins, enzymes, and genes.[8] Materials such as enzymes or drugs can be brought into a form of core template or be attached to a core template particle prior to core decomposition so as to trap them inside hollow capsules.[9] To load macromolecules into the pre-formed capsules, efforts were made by using in situ polymerization of monomers inside the capsules by applying a "ship in bottle" synthesis or by changing the permeability of the capsule wall at different pH.[10] The recent novel finding that various water-soluble substances can spontaneously deposit into the interior of the pre-formed capsules inspires a most convenient and effective way to incorporate bioactive macromolecules.[11]

Entities with large geometric size and rigid structure such as nanoparticles and macromolecules of ultrahigh molecular weight are difficult to incorporate unless one takes specific measures to open the capsules (Scheme 1). Such a measure is achieved in this work by heating the capsules moderately and by applying high ionic strength. We show here that the process

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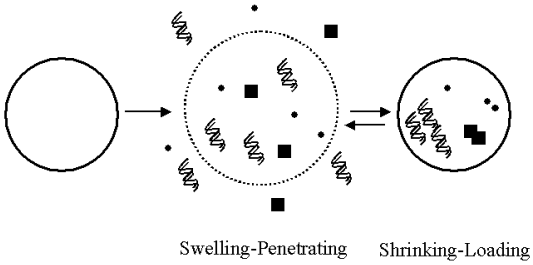

Scheme 1. Schematic representation to show the convenient encapsulation of materials inside the polyelectrolyte capsules with swelling and shrinking. In the swollen state, an enlarged pore size in the capsule wall can be expected to permit materials to penetrate, where after shrinking the penetration will be forbidden resulting in materials loading.

is reversible, that is, holes created are disappear again returning to the starting conditions. The efficiency of the process will be quantified in future work.

The typical hollow polyelectrolyte capsules produced so far were composed of alternating poly(styrenesulfonate sodium salt) (PSS) and poly(allylamine hydrochloride) (PAH). Recently, instead of PAH, another polycation, poly(diallyldimethyl ammonium chloride) (PDADMAC), was employed for the preparation of PSS/PDADMAC capsules.[12] Preliminary studies revealed that PSS/PDADMAC capsules possess larger swelling during the core decomposition process, a larger size than the template core, a rougher surface topology, and a lower elasticity.[5, 12] These differences suggest that the structure of the PSS/PDADMAC capsules may be more susceptible to environmental influences, thus providing the possibility of swelling and shrinking under some conditions.

Herein we report the response and structure variation of these newly composed capsules consisting of PSS and PDADMAC to annealing and electrolyte incubation. We observe interesting changes upon annealing and high sensitivity to the addition of electrolytes. A large extent of capsule swelling occurred upon annealing, while capsule shrinking occurred upon salt incubation. It also shows that capsules with versatile properties could be easily obtained through simply changing the components.

Results and Discussion

The size of PSS/PDADMAC capsules determined during the core decomposition process was found to be apparently larger than that measured afterwards. Evidently, some shrinkage of capsules occurred afterwards. One can assume that the capsule wall undergoes changes in time. This seems to be a very general feature of polyelectrolyte capsules templated on MF particles. For example, when PSS/PAH capsules were heated the capsule size decreased, but the density and the volume of the capsule wall remained approximately constant.[7] It can be assumed that this change is caused by a rearrangement of the layer constituents. For this to occur it is necessary that the ion pairs formed between oppositely charged polyelectrolytes, which are responsible for the stability of the layer, change; breaking and reforming yields a different arrangement of the layer-forming polymers. Heating should facilitate the transient breaking of electrostatic bonds between oppositely charged polyelectrolyte groups.

That PSS/PDADMAC capsules may be qualitatively different from PSS/PAH capsules is indicated by the fact that PSS/PAH capsules are of the size of the template, while the PSS/PDADMAC capsules are larger than the template. The mean diameter is 5.5 μm (Figure 1a and Table 1), while the diameter of the template is 3.8 μm. Thus it was intriguing to study annealing of PSS/PDADMAC capsules.

Surprisingly, when the capsules were incubated in H_2O at 40 °C for 2 h the capsule size increased to 7.5 μm (Figure 1b and Table 1). Such a behavior is opposite to that of PSS/PAH capsules, where shrinking was always observed. In parallel with the capsule volume increase the capsule wall becomes thinner (Table 1). It was further remarkable that PSS/PDADMAC capsules were unstable at 70 °C. Incubation at this temperature induced breaking of the PSS/PDADMAC capsules. The spherical shape converted to an open cup or pancake-like polyelectrolyte film.

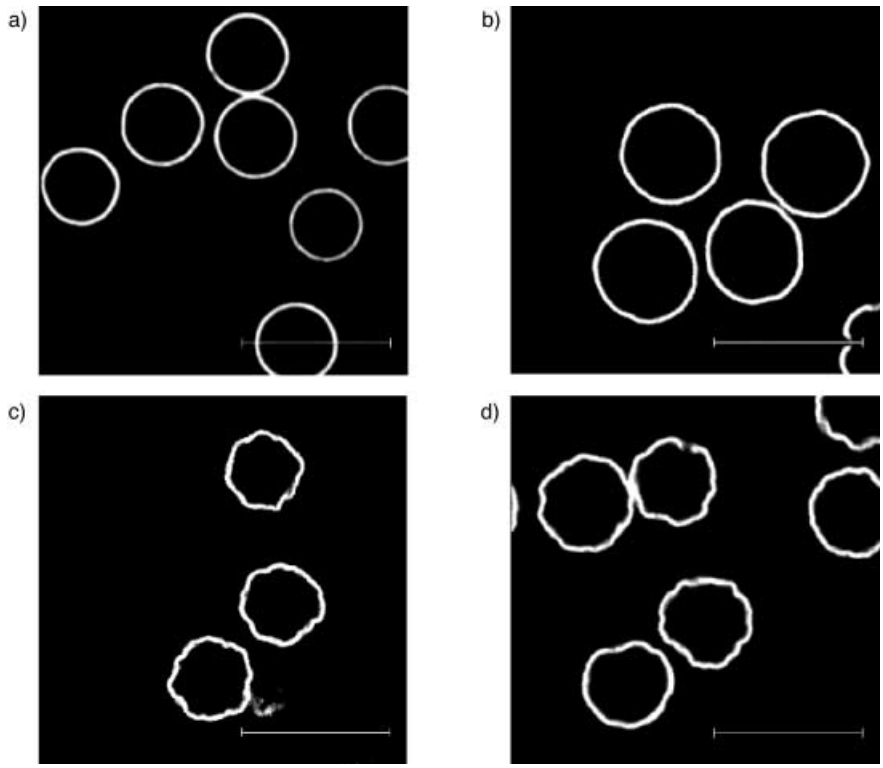

Figure 1. CLSM images of $(PSS/PDADMAC)_5$ capsules with an initial diameter of 5.5 μm (core size 3.8 μm). a) Control, b) annealing at 40 °C for 2 h, c) cooling of (b) overnight, and d) re-annealing of (c) at 40 °C for 2 h. All the CLSM images herein have the same magnification for direct comparison. Scale bar 10 μm.

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Table 1. The sizes, wall thicknesses, relative surface areas, and relative wall volumes of $(PSS/PDADMAC)_5$ capsules upon annealing and salt-exposure, as determined from CLSM and SFM measurements.

Samples	Capsule diameter[d] d [μm]	Wall thickness[e] 2δ [nm]	Relative surface area[f]	Relative wall volume[g]
control[a]	5.5 ± 0.2 (5.7 ± 0.3)	43	1	1
annealed[b]	7.5 ± 0.37 (8 ± 0.3)	20	1.86	0.87
annealed & cooled	5.5 ± 0.2		1	
annealed, cooled & re-annealed	6.6 ± 0.2		1.44	
albumin exposed	4.4 ± 0.1 (4.4 ± 0.2)	80	0.64	1.18
electrolyte exposed[c]	3.4 ± 0.1 (3.8 ± 0.2)	72	0.38	0.63
electrolyte exposed & annealed	2.6 ± 0.1 (3.2 ± 0.2)	108	0.22	0.54

[a] The core diameter is 3.8 μm. [b] At 40 °C for 2 h. [c] In 0.5 M sodium chloride solution for 2 h. [d] Data out and in parentheses were from CLSM and SFM, respectively. [e] Wall thickness determined by SFM (see Figure 4). [f] Data calculated by the capsule diameter from CLSM. The capsule surface area of the control was assigned to 1. [g] Data calculated by the capsule diameter from CLSM and capsule wall thickness from SFM according to $V = \frac{1}{3}\pi[(d/2)^3 - (d/2 - \delta)^3] \approx \pi d^2\delta$. The capsule wall volume of the control was assigned to 1.

As annealing induces capsule swelling, one may expect that cooling, on the other hand, could cause capsule shrinking. It was observed that the annealed capsules recovered their original size after they were cooled at 4 °C overnight, but more creases on the capsule surfaces appeared (Figure 1c and Table 1). As a comparison, both the diameter and the shape of the cooled capsules without prior annealing showed no difference from the control either in the wet state or in the dry state. Due to the abundant local curvature changes it is not clear whether the "real area" follows that of the diameter. The annealed and cooled capsules expanded again when they were re-annealed at 40 °C (Figure 1d and Table 1). The creases did not disappear completely, but the capsule diameter (6.6 μm) was slightly smaller than that of the first annealing. The creases on the surfaces of the annealed and cooled capsules may be produced by the inhomogeneous shrinkage of the capsule wall in the cooling procedure. This phenomenon suggests that cooling of the annealed capsules can also induce permanent microstructure rearrangement of the capsule wall. Some electrostatic bonds might have been formed between the constituent polyelectrolytes of the annealed capsule wall, while they encountered inhomogeneous shrinking during cooling. Re-annealing did not totally remove the curvature changes.

Scanning force microscopy (SFM) investigations proved that the creases and folds of the continuous polyelectrolyte films (Figure 2a), which were introduced by the collapse of the films after evaporation of the aqueous content, were preserved after annealing (Figure 2b). A small number of polyelectrolyte capsules were destroyed upon temperature increasing. The statistical capsule diameters of the control and the annealed capsules from SFM images (Table 1) were consistent with the data from CLSM, which further demonstrated capsule expansion occurred upon annealing in water.

The capsule wall volume was estimated via the capsule diameter from CLSM and capsule wall thickness from SFM. Volume reduction by up to a factor of two was found after annealing (Table 1). Possible reasons are the material loss or/and material compression during the annealing process. Single particle light scattering (SPLS) measurement revealed that the relative mass of the capsules after annealing was 0.84, which was quite consistent with the volume reduction. Moreover, small pieces of polyelectrolyte films can be observed under CLSM after annealing. All these results prove that material loss happened upon annealing. The mechanism might be dissolution as a result of bond breaking occurring while the sample was kept at elevated temperature. By contrast, no material loss was found for PSS/PAH capsules upon annealing.[7] This difference further revealed the different characteristics of the two kinds of capsules, which should be attributed to the different positively charged components, that is, PAH and PDADMAC. It suggests that the coupling of PDADMAC and PSS is much weaker than that of PAH and PSS.

PSS/PDADMAC capsules thus obtained are positively charged if PDADMAC is the outermost layer. Preliminary studies revealed that a variety of charged compounds have a strong interaction with PSS/PAH capsules. For example, proteins, dyes, and lipid vesicles are readily adsorbed onto the capsule walls. Interestingly, a significant diameter reduc-

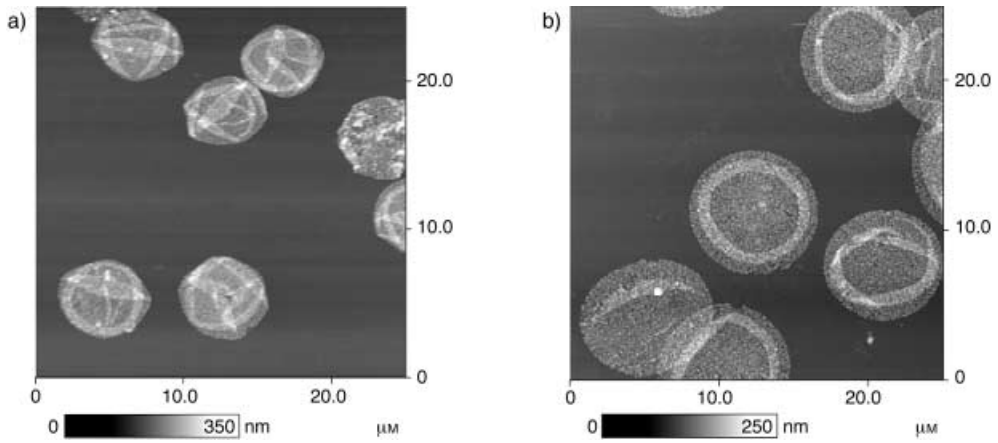

Figure 2. SFM images of $(PSS/PDADMAC)_5$ capsules. a) Control; b) annealing at 40 °C for 2 h.

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tion was found when PSS/PDADMAC capsules were incubated with the zwitterionic fluorescein isothiocynate-labeled albumin (FITC-albumin) (Figure 3a), weak polyelectrolyte, which was frequently used to label polyelectrolyte capsules consisting of PSS/PAH for the convenience of observation under CLSM in the elasticity measurement.[6, 12] In this case a size variation was not observed. However, after incubation of PSS/PDADMAC capsules with FITC-albumin, the capsule diameter decreased from 5.5 μm to 4.4 μm accompanied by a capsule wall thickness increase (Table 1). The capsules collapsed to form perfect polygonal shapes with folds after the water content was evaporated as shown in Figure 3b. The estimated relative wall volume was slightly larger than that of the control. This may be caused by the adsorption of albumin. These findings underlie the sensitivity of the capsules toward the nature of the top layer. Obviously, the introduction of albumin was sufficient to induce a change in the layer properties throughout the layer.

Pronounced diameter reduction was found when PSS/PDADMAC capsules were exposed to concentrated electrolyte solution, that is 0.5 M NaCl at room temperature. The CLSM image shows that the spherical shape of the capsules is largely preserved (Figure 3c). The SFM characterization proves further that the reduction of the capsule diameter in the dry state is quite consistent with that in the wet state from CLSM (Table 1). In parallel with the shrinkage in the diameter of the capsule, the capsules increased their wall thickness. The more the diameter reduced, the more the wall thickness increased. It is worth noting that the capsule shrinking caused by salt addition is irreversible. The reduction of capsule diameter caused a dramatic decrease of the capsule surface area to around one third for capsules treated with salt at 23 °C (Table 1). It is remarkable that the size of the capsules became almost identical to that of the templates. Probably, the capsule in salt solution was sufficient to remove the osmotic stress-induced expansion, which occurred during core dissolution.[12] This feature indicates that electrostatic conditions play an important role for the topology of PSS/PDADMAC capsules. A few observations support this view; for example, the thickness of 10 layers of PSS/PAH polyelectrolyte multilayers deposited on solid substrate changed from 48 nm initially to 41 nm after the multilayers were incubated with 0.75 M NaCl.[13] If the salt incubation would have induced large volume changes as shown in Table 1, that is, compression of the wall, this should influence on the elastic properties. Hence, the elasticity modulus of the PSS/PDADMAC multilayers has been measured by using the osmotically induced invagination after the capsules were incubated in 0.1M NaCl solution. The derived value, 321 MPa, is doubled compared to that of the control (140 Mpa).[6] This increase of the elasticity modulus should be exclusively attributed to the occurrence of the multilayer compression, leading to a denser layer architecture.

Interestingly, the capsule size decreased further when PSS/PDADMAC capsules were treated in salt solution and at an elevated temperature simultaneously (Figure 3d). Characterization by SFM revealed that the capsule wall thickness increased further from 36 nm (salt-exposed only) to 54 nm (Figure 4a and Figure 4b). This structure rearrangement leads to a further reduction of the surface area to one fifth and the wall volume to one half of the control. Notably, still longer incubation in salt solution up to 20 h did not lead to a further reduction in size, while the swollen capsules after annealing can be shrunk again if they are treated with salt solution; for example, reductions of 1.27 μm and 1.43 μm were found for swollen capsules (5.76 μm) treated with a 0.1M NaCl solution for 2 h at room temperature and 40 °C, respectively.

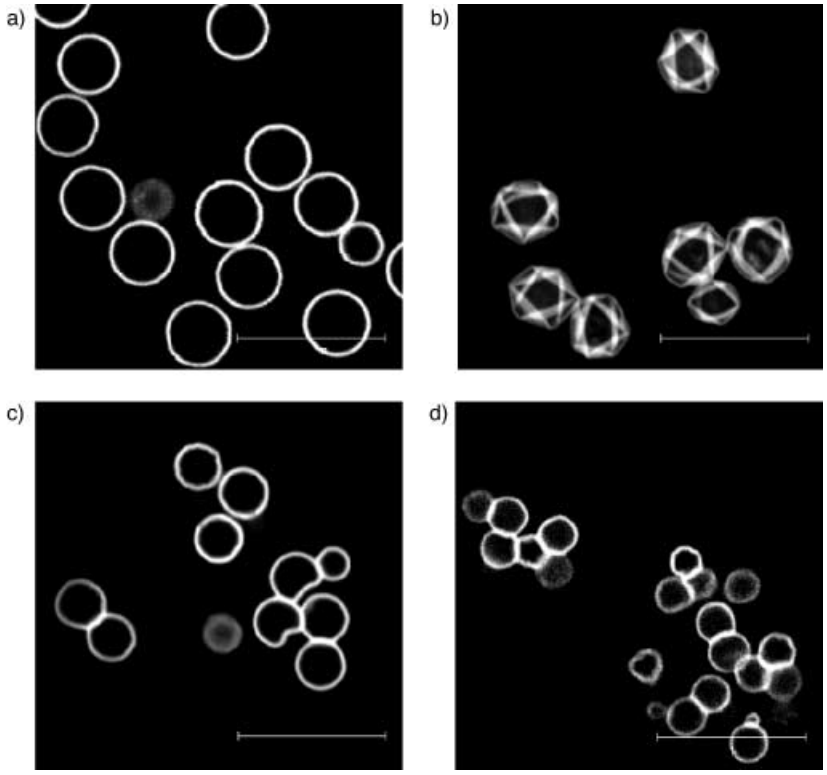

Figure 3. CLSM images of $(PSS/PDADMAC)_5$ capsules. a) Incubated in 0.5 mg mL^{-1} FITC-albumin solution at 4 °C for 2 h; b) dry state of (a), treated in 0.5 M NaCl for 2 h at 25 °C (c) and 40 °C (d) , respectively. Scale bar 10 μm.

The presented results show that the PSS/PDADMAC capsule wall is a rather sensitive structure. Changes in salt concentration, in temperature, and in adsorption influence the capsule size, shape, and wall thickness. The degree of the observed changes is remarkably large. The behavior is more complicated than previously observed for PSS/PAH capsules, where so far only shrinking has been found as a result of annealing.[7] How can this behavior be explained? Certainly, the interaction of PDADMAC with PSS provides the key for the understanding of the behavior of the system.

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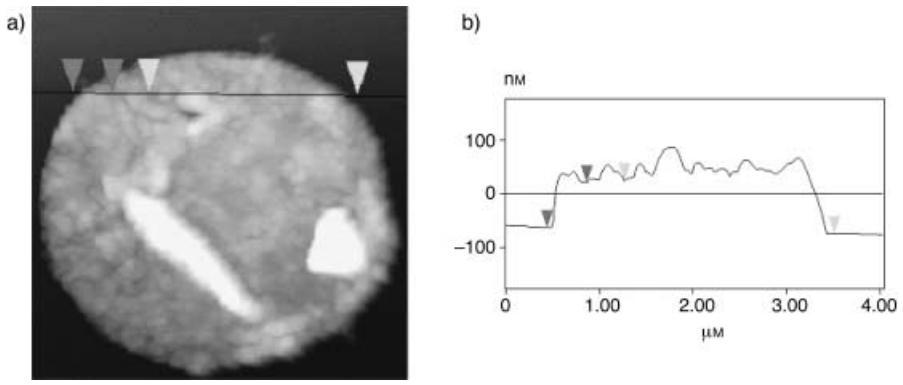


Figure 4. a) SFM image of $(PSS/PDADMAC)_5$ capsules upon treatment in 0.5 M NaCl at 40 °C for 2 h. b) Cross-section profile as shown in (a) to display the huge increase of the capsule wall thickness.

The structure of the PSS/PDADMAC capsule wall can be assumed to be a highly coiling layer, in which irregular pores are distributed through the entire multilayers. This is evidenced by the fact that the capsules are freely permeable for macromolecules with ultrahigh molecular weight (dextran, $M_w = 2000$ kDa).[14] The multilayer is held together by randomly distributed electrostatic bonds. Probably, a number of fixed charges are not able to form ion pairs because of topological restrictions brought about by the two bulks and stiff polymers. This is supported by the fact that the bond density of the PSS/PDADMAC complex is as low as 0.0625 ion pair per C atom, in contrast to a value of 0.11 found in PSS/PAH multilayers.[15] This indeed indicates a smaller crosslinking density, suggesting that the PSS/PDADMAC multilayers are more loosely interconnected than in the case of PSS/PAH multilayers. Together with the mismatch of the charges along the PDADMAC and PSS chains, the PSS/PDADMAC multilayers constructed in this way provide the possibility for the corresponding capsules to be sensitive to environmental stimulation; for example, varying their structure upon annealing and salt-exposure.

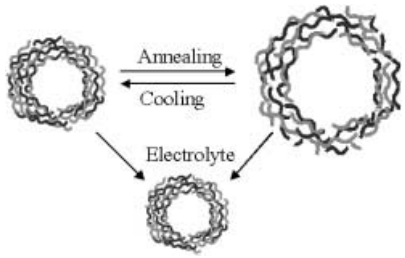
A rather important point is that PDADMAC and PSS are adsorbed in 0.5 M NaCl. Accordingly, the structure of PDADMAC and PSS in the layer can be assumed to be a flat coil, because in solution (prior to adsorption) counterions largely reduce intramolecular repulsion. In water these molecules would adopt a more rodlike shape. The elevated temperature generally facilitates the thermal motion of the polymer segments, and the probability for bond breaking increases. During the annealing process, the unbonded segments should move in the direction of increased entropy. This would correspond to a more three-dimensional structure of the layer constituents resulting in an increase in the layer thickness together with a decrease in the diameter of the capsule. This behavior was discussed in detail for PSS/PAH capsules, and is found here only when the annealing takes place in the presence of salt. However, when the annealing takes places in water a large expansion of the layer is observed for PSS/PDADMAC capsules. This behavior is contrary to what one would expect from entropy considerations.

The influence of the salt, however, immediately points to the electrostatic nature of the process. In water, as mentioned above, the highly charged PDADMAC (in contrast to the weakly charged PAH) should assume a rigid-rod structure. Hence, the structure of the out of a salt solution adsorbed PDADMAC is inconsistent with equilibrium when the capsules are incubated in salt free solution. Probably, the top layer or the innermost PDADMAC tends to elongate driven by the repulsion of non-compensated charges. Since it is complexed to PSS this tendency should result in an overall multilayer expansion in the absence of NaCl. We can thus conclude that electrostatics overrides entropy effects.

It is quite likely that the temperature-induced elongation or coiling tendency of PSS and PDADMAC is not equal, since there is a mismatch of monomer length and a different stiffness (the quaternary amino groups cannot freely rotate). Evidently, elongation or coiling of one layer is different from the adjacent neighbor. This would introduce bending. If there is even a slightly inhomogeneous distribution in the plane, local changes of capsule curvature are expected to occur. This is indeed the case, as evidenced after cooling and reannealing. The adsorption and possible partial penetration of albumin influence on the charge balance in the layer. It may thus introduce layer rearrangements toward an entropically favored state, as evidenced from the shrinking provided in Table 1.

Conclusion

We have shown that PSS/PDADMAC multilayer microcapsules are sensitive to annealing and cooling, as well as to electrolyte exposure (Scheme 2). Incubation of the capsule suspension at an elevated temperature induces apparent capsule swelling, while the swollen capsules can reversibly shrink after cooling. On the other hand, electrolyte exposure causes pronounced permanent reduction of the capsule size in parallel with capsule wall compression, leading to a stronger mechanical stability against deformation. This high sensitivity of the microcapsules to the environmental stimulation is



Scheme 2. Schematic illustration of the PSS/PDADMAC capsules swelling and shrinking as a result of increasing the temperature and exposing to an electrolyte, respectively. Annealing causes the capsule to increase in size, while cooling of the annealed capsule induces reversible shrinking. On the other hand, both the control and the annealed capsules decreased considerably in size upon treatment with electrolyte solution.

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attributed to the porous microstructure of its constituents, the PSS/PDADMAC multilayers, and the weak bonds of the ion-pairs between PDADMAC and PSS. The special swelling–shrinking behavior of the capsules may benefit the loading of substances such as nanoparticles and macromolecules with rigid structure or larger molecular size. This could result in capsules for versatile applications as microcarriers in fields of drug delivery and controlled release, catalysis, as well as artificial cells.

Experimental Section

Materials: The sources of chemicals were as follows: PSS, $M_w \sim 70000$, and PDADMAC, Medium $M_w \sim 200-350$ kDa (20 wt% in water), Aldrich; weakly crosslinked melamine formaldehyde particles (MF-particles), microparticles GmbH, Germany. All chemicals were used as received. The water used in all experiments was prepared in a three-stage Millipore Milli-Q Plus 185 purification system and had a resistivity higher than 18.2 MΩ cm.

Capsule and multilayer preparation: A membrane filtration technique was employed to consecutively adsorb PSS and PDADMAC onto melamine formaldehyde (MF) resin particles (MF particles).[16] The adsorption of polyelectrolyte (1 mg mL^{-1}) was conducted in NaCl solution (0.5 mol) for 5 min, followed by three washings in H_2O. Then the respective oppositely charged polyelectrolyte species was adsorbed. After the desired number of layers was adsorbed the coated particles were treated in HCl solution (pH 1.1) to decompose the MF cores. The produced MF decomposition products and excess HCl were washed off until neutral pH was established by filtration with gentle agitation. The outermost layer in this study is always the positively charged PDADMAC.

Annealing and incubation in salt solution: Suspensions of capsules in water and in NaCl solution (0.5 mol) were incubated for 2 h at 40 °C to obtain the annealed samples. The controls were kept at room temperature (25 °C). After incubation the salt was removed by centrifugation (1145 g) and three subsequent washings in H_2O.

FITC-albumin-labeled capsules: Equal amounts of capsule suspension and FITC-albumin solution (1 mg mL^{-1}) were mixed and incubated for 2 h at 4 °C. The suspension was centrifuged (1145 g) and washed three times in H_2O to remove the excess FITC-albumin.

Confocal laser scanning microscopy (CLSM): Confocal micrographs were taken with the Leica TCS NT (Leica, Germany), equipped with a 100 × oil immersion objective. 6-Carboxyfluorescein (6-CF) was used as a label to visualize the capsules to allow their sizes and shapes to be determined. The capsule solution and 6-CF were mixed on a glass cover slip. The images of capsules in aqueous environment were acquired immediately. The images in the dry state were taken after the water had evaporated.

Scanning force microscopy (SFM): SFM images were recorded in air at 20–25 °C using a Nanoscope III Multimode SFM (Digital Instrument Inc., Santa Barbara, CA). The samples were prepared by applying a drop of the capsule solution onto freshly cleaved mica. The layer thickness was measured from the flat regions in the profiles (Figure 4b) with an accuracy of 10%. To compare with the result in solution from CLSM, the apparent capsule "diameter" was also measured from the collapsed contours by SFM (viewed perpendicular) with an accuracy of 5 ~ 10%.

Single particle light scattering (SPLS): SPLS measurements were conducted on a home-built photometer equipped with an argon laser (Innova 305 from Coherent) with power track. The dispersion was pressed through a thin capillary with an orifice of 0.1 mm at the end. Hydrodynamic focusing was applied. The capsule concentration was adjusted to minimize the coincidence of the scattering from individual particles. The light pulses recorded from capsules flowing through the scattered volume were detected at angles between 5° and 10° (forward scattering).

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